Molecular Structure of Gaseous Oxalic Acid

from Electron Diffraction and IR Data

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Gaseous oxalic acid has been studied by IR and electron diffraction. In the IR spectrum, the $O-H$ stretching vibration band is shifted to 3475 cm⁻¹, and accordingly the molecule possesses two weak intramolecular hydrogen bonds. The molecule must therefore be in a *trans* conformation with the hydrogen bonds pointing toward the neighbouring carbonyl oxygens, and the intramolecular hydrogen bonds are closing five-membered rings. The electron diffraction investigation gives a planar *trans* conformation (C_{2h}-symmetry) with the following parameters: $r(C-C) = 1.548(0.004)$ Å, $r(C=O) = 1.208(0.001)$ Å, $r(C-O) = 1.339(0.002)$ Å, $r(O-H) = 1.056(0.014)$ Å, $\angle C-C=O = 123.1(0.9)°$, $\angle O=C-O = 125.0(0.2)°$, and $\angle C-O-H = 104.4(2.3)°$. r_a distances obtained by the least-squares method are given, and numbers in parenthesis are standard deviations obtained by least-squares refinements applying a weight matrix with off-diagonal elements to include effects from correlated errors in the data. The best values of the other structure parameters experimentally determined in this investigation are given in column a_2 of Table 1 and Table 2.

$\mathbf{S}$olid anhydrous oxalic acid exists in α and β modifications, and the structures of these forms are known from X-ray investigations [1,2] and IR studies.[3] The free molecule was studied by electron diffraction in 1954.[4] According to these studies, the molecule is in a planar *trans* conformation, and the central $C-C$ bond has no double bond character.

However, it seemed of interest to reinvestigate this structure to obtain more accurate parameters for the free molecule including the positions of the hydrogen atoms. It was hoped that this would lead to some more information about the effect of the hydrogen bond environment upon the structure of the carboxyl group.

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IR SPECTRUM OF GASEOUS OXALIC ACID

Anhydrous oxalic acid was purified by vacuum sublimation at about 150°C. The water content was checked by Karl Fischer titrations, and it never exceeded 0.1 %. (The sample used in the electron diffraction investigation was purified in the same way.)

The infrared spectrum was recorded with a Perkin-Elmer model 225 spectrometer. A heated cell from RIIC with a beampath of 9 cm, equipped with KBr windows and a thermocouple, was employed for the vapour study. The cell was heated and evacuated before transferring the sample. This was carried out in a dry-box, and the spectrum was recorded at 150°C.

In recording the spectrum, several experimental difficulties were met: 1. On heating crystals and vapour of oxalic acid, it decomposes to formic acid, carbon dioxide, and water, as reported previously.[5] 2. The oxalic acid reacted with the KBr of the cell window.[6] 3. The vapour condensed on the windows as crystals.

Although the experimental conditions were modified to eliminate these complications, the total absence of effects from these factors cannot be guaranteed, and the only certain conclusion that could be drawn from the IR investigation is that the absorption band at 3475 cm^{-1} corresponds to the $O-H$ stretching vibration band of gaseous oxalic acid, signifying weak intramolecular hydrogen bonds.[7] No band was then observed in the wave number range of a free $O-H$ group.

ELECTRON DIFFRACTION INVESTIGATION

Diffraction photographs from the Oslo apparatus [8] for a nozzle temperature of about 160°C, and for an electron wave length of 0.064890 Å, corresponding to an accelerating voltage of approximately 36 kV were obtained. Four photographic plates for each of the two camera distances of about 48 and 20 cm were used for the structure investigation.

The plates were photometered, and the data were processed and analyzed in the usual way.[9] Partial waves scattering factors computed for 35 kV electrons [10] based upon analytical HF potentials of the atoms [11] were applied. The best radial electron density of bonded hydrogen as given in Ref. 12 was used in computing the scattering factor for this atom. The first backgrounds were drawn on the levelled intensity curves, and the molecular intensities obtained were modified by $s/|f_C'|^2$.

The four intensity curves for each camera distance were put on a common scale, averaged and connected, and radial distribution functions were computed. Least-squares refinements for a planar *trans* conformation converged after some difficulties, and good agreement with the experimental data was then obtained. The background was adjusted and other models were tried. Refining the torsional angle about the central $C-C$ bond, this angle converged to a value not significantly different from zero. A planar *cis* conformation gave significantly poorer agreement than the *trans* conformation.

Two different models were tried for the positions of the hydrogen atoms. In the first model, the $O-H$ bonds pointed toward the neighbouring carbonyl oxygens, and a hydrogen bond would here close a five-membered ring. The second model was obtained from the first one by rotating the hydrogen atoms 180° around the $O-C$ bonds. This model is not advantageous for forming intramolecular hydrogen bonds, as these bonds now will have to close four-membered rings. The two models fitted the data just as well. For the second model, the results were slightly inconsistent as the obtained $O-H$ distance
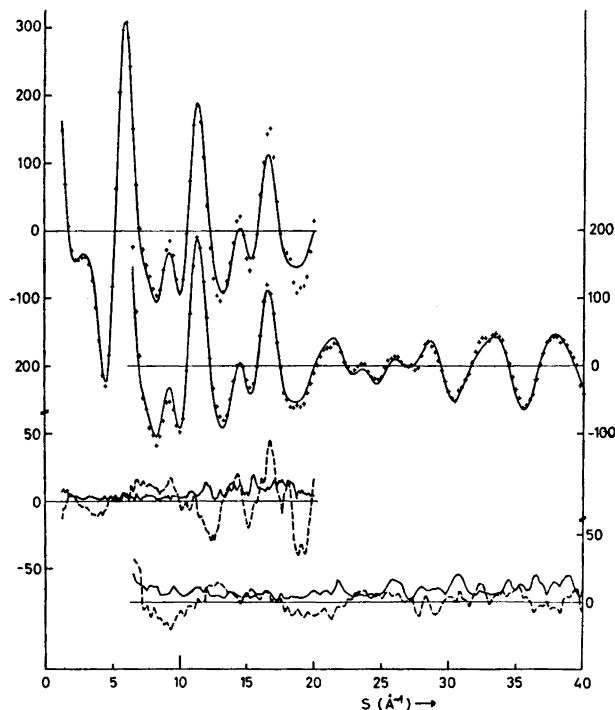
Fig. 1. $s/|f_C'|^2$-modified molecular intensities for oxalic acid. The two upper curves are experimental (crosses) and theoretical (drawn) intensities for the data from the 48 cm camera distance from $s=1.25$ to $s=20$ in intervals of $\Delta s=0.125$ Å^{-1}, and for the 20 cm camera distance from $s=6.5$ to $s=40$ for $\Delta s=0.25$ Å^{-1}. The theoretical curves are computed for the parameters given in column a_2 of Tables 1 and 2. The two lower curves are the differences between the observed and computed intensities (broken curves) and the standard deviations of the average intensities from the four single measurements (drawn curves). Note that the scale of the two lower curves has been doubled in relation to the two upper curves.

was longer than the value expected in a free O$-$H group while this model should not allow formation of intramolecular hydrogen bonds. This observation was hardly significant, but the second model is certainly not consistent with the results of the IR investigation and can be rejected for that reason.

Having established the molecular structure, the backgrounds were adjusted on the four intensity curves from each camera distance, and the curves were scaled appropriately. The standard deviations in each point of the average curve, σ_j, and the average correlation coefficients, $\varrho(|s_k - s_l|)$, were estimated.[13]

If the error distribution is represented by a normal, multivariate probability density, then the weight matrix in the least-squares procedure should be given by $P = \sigma_0^2 M^{-1}$ where M is the moment matrix of the observations. The elements of P may be written

$$P_{kl} = \sigma_0^2 (\sqrt{w_l}(\varrho^{-1})_{kl}\sqrt{w_k}) \tag{1}$$

where the w_j's are elements of a normalized diagonal matrix, each element proportional to $1/\sigma_j^2$. In the present procedure, the w_j's are approximated by $w = \exp(-k_1(s-s_1)^2)$ for $s < s_1$ and with a corresponding expression for $s > s_2$, for $s_1 \leq s \leq s_2$, $w = 1$.[9] The constants s_1, s_2, k_1 and k_2 were chosen to make w approximately proportional to $1/\sigma_j^2$ for the σ_j's illustrated in Fig. 1. The applied values for the constants are given in the captions of Table 1 for the data from the two camera distances.

The correlation in the data is described by ϱ. The approximations that $\varrho_{kl} = \varrho(|s_k - s_l|)$, and that $(\varrho^{-1})_{kl} = p_{1+|k-l|}$, with the constants p_i nonzero only for i $\leq$ 3 and normalized to $p_1 = 1$, were applied.[13] The values of $\varrho(|s_k - s_l|)$ computed from the data and the values of ϱ obtained by inverting the matrix with the three nonzero constants $p_{1+|k-l|}$ are illustrated in Fig. 2, and the values of the p_i's are given in the captions of Table 1.
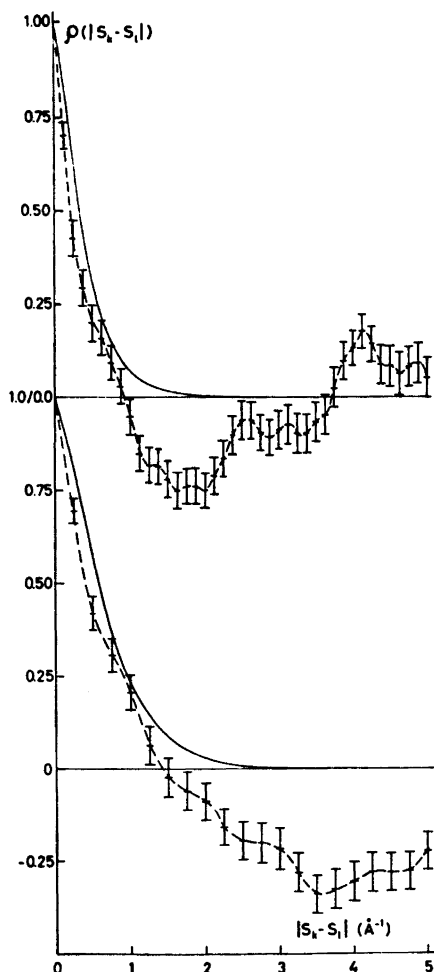

Fig. 2. Average correlation coefficients $\varrho(|s_k - s_l|)$ and their standard deviations (vertical bar) from the experimental data. The drawn curves are obtained by inverting the matrix $p_{1+|k-l|}$ for the three nonzero p_i's given in Table 1, and these curves represent the correlation included in the weight matrix. Upper part is for the data from the 48 cm camera distance, and lower part for the data of the 20 cm camera distance.

Table 1. Least-squares results for the distances, angles and scale factors of oxalic acid.

	a_1	a_2	b_1	b_2	c_2	c_3
$r(C-C')$	1.5489(0.0024)	1.5478(0.0037)	1.5444(0.0035)	1.5432(0.0057)	1.5576(0.0035)	1.5546(0.0042)
$r(C=O_2)$	1.2069(0.0008)	1.2076(0.0012)	1.2052(0.0009)	1.2064(0.0016)	1.2099(0.0013)	1.2110(0.0019)
$r(C-O_1)$	1.3405(0.0010)	1.3390(0.0015)	1.3377(0.0012)	1.3368(0.0020)	1.3423(0.0016)	1.3442(0.0032)
$r(O_1-H)$	1.0358(0.0076)	1.0556(0.0142)	1.0259(0.0079)	1.0495(0.0160)	1.0643(0.0152)	1.0394(0.0157)
ϕ_1	56.50(0.74)	56.94(0.94)			55.75(0.68)	56.44(0.96)
ϕ_2	68.37(0.72)	68.04(0.92)			69.24(0.67)	68.39(0.98)
ϕ_3	103.40(1.49)	104.37(2.29)			106.53(2.67)	105.22(1.49)
$r(C\cdots O_2')$	2.4329(0.0087)	2.4276(0.0112)	2.4383(0.0246)	2.4481(0.0297)	2.4463(0.0073)	
$r(C\cdots O_1')$	2.3930(0.0103)	2.3954(0.0130)	2.4043(0.0190)	2.3857(0.0288)	2.3817(0.0101)	
$r(O_1\cdots O_2)$	2.2591(0.0015)	2.2596(0.0021)	2.2650(0.0048)	2.2615(0.0033)	2.2586(0.0022)	
$r(O_2\cdots O_2')$	3.5146(0.0118)	3.5082(0.0150)	3.5142(0.0153)	3.5113(0.0164)	3.5215(0.0097)	
$r(O_1\cdots O_2')$	2.7197(0.0036)	2.7169(0.0047)	2.7384(0.0049)	2.7269(0.0067)	2.7226(0.0044)	
$r(O_1\cdots O_1')$	3.5563(0.0138)	3.5590(0.0175)	3.5483(0.0254)	3.5501(0.0263)	3.5119(0.0138)	
$r(C\cdots H)$	1.8743(0.0194)	1.8996(0.0287)			1.9350(0.0334)	
$r(C\cdots H')$	2.1943(0.0339)	2.2184(0.0483)			2.2305(0.0504)	
$r(H\cdots O_2)$	3.0242(0.0168)	3.0509(0.0246)			3.0654(0.0287)	
$r(H\cdots O_2')$	2.0393(0.0259)	2.0441(0.0402)			2.1015(0.0436)	
$r(H\cdots O_1')$	3.5184(0.0342)	3.5427(0.0482)			3.5224(0.0502)	
$r(H\cdots H)$	3.7758(0.0569)	3.8294(0.0822)			3.8263(0.0900)	
k_1	4.8072(0.0543)	4.6506(0.0829)	4.7808(0.0532)	4.6291(0.0867)	4.6584(0.0890)	
k_2	4.9346(0.1152)	4.6381(0.1596)	4.8830(0.1122)	4.5860(0.1664)	4.6558(0.1596)	
$\mathbf{V'PV}\times10^{-3}$	18.025	1.915	16.666	1.880	2.014	

r_a distances in Å and angles ϕ in degrees. Numbering of the atoms, and definition of the angles are illustrated in Fig. 3. k_1 and k_2 are the scale factors for the data from the 48 cm camera distance and from the 20 cm one respectively, and $\mathbf{V'PV}$ is the weighted square error sum. The diagonal part of the weight matrix for the data from the 48 cm camera distance was for $s<2$, $w=\exp[-2.2(2-s)^2]$, $2\leqq s\leqq10$, $w=1$, and for $s>10$, $w=\exp[-0.043(10-s)^2]$, and for the 20 cm camera distance data, $s<9$, $w=\exp[-0.61(9-s)^2]$, $9\leqq s\leqq25$, $w=1$, and for $s>25$, $w=\exp[-0.006(25-s)^2]$.

For columns indexed 1 this diagonal matrix was applied. In the columns indexed 2, off diagonal elements were included with $p_1=1$, $p_2=-0.6$, and $p_3=0.110$ for the data from the 48 cm camera distance and $p_1=1$, $p_2=-0.6$, and $p_3=0.115$ for the 20 cm camera distance data. In all the refinements the u-values involving hydrogen atoms were fixed on the computed values given in the captions of Table 2, the other u-values were varied and the results are given in Table 2.

a. The planar *trans* model as illustrated in Fig. 3 was used as restraint, then of the geometric parameters, only $r(C-C')$ to ϕ_3 were independent.

b. No geometric restraint was applied. The nonbonded distances involving hydrogen atoms were fixed on the values obtained in a_2.

c_2. The geometry of the planar *trans* model was fulfilled by the r_α distances rather than the r_a-distances. The values given are r_a distances.

c_3. Average values of the four refinements for data based on one single plate for each of the two camera distances, and standard deviations estimated according to eqn. 2. The weighting and refinement scheme were as for c_2.

The constant σ_0 for the data from each of the two camera distances may be estimated from the average values of σ_j between s_1 and s_2 and from the normalization constant of ϱ^{-1}. This gives $\sigma_0\approx1.4$ for the data from the camera distance of 48 cm and $\sigma_0\approx2.1$ for the 20 cm data.

The final least-squares refinements were carried out on the two average intensity curves, keeping the curves separated and refining one scale factor for each of the two curves.[14] The data from the 20 cm camera distance should then, relative to the data from the 48 cm one, be weighted down by a factor equal to the ratio between the squared σ_0's, $(1.4)^2/(2.1)^2 = 0.44$. If this is done, the standard deviations of the parameters are slightly larger than when the two data sets are given the same relative weights, and it is much more difficult to make the iteration converge. For the different least-squares results reported in Tables 1 and 2, the two data sets have therefore been given the same relative weights.
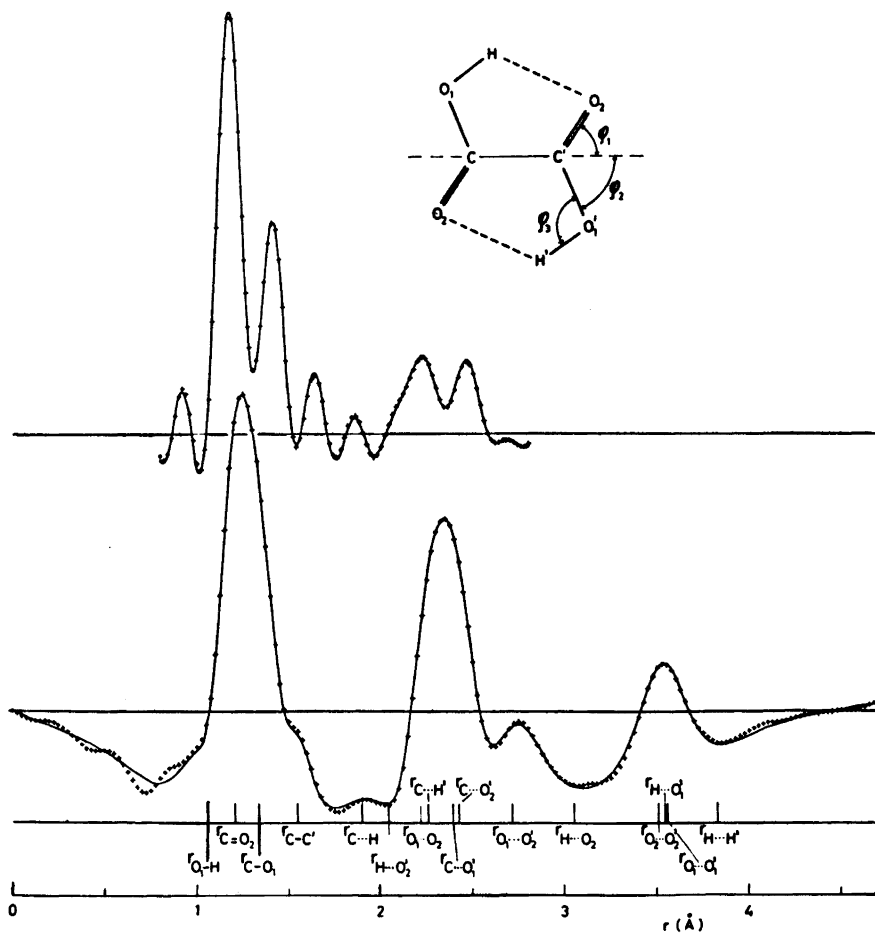

Fig. 3. Numbering of the atoms and definition of the angles in oxalic acid. Upper curve is the autocorrelation power spectrum and lower curve is the radial distribution function obtained by damping the intensities with the function $\exp(-0.002\ s^2)$. Points computed from the experimental data (crosses), and from the parameters of column a_2 in Tables 1 and 2 (drawn curves) are given.

Table 2. Least-squares result for u-values including u- and K-values computed for an approximate valence force field of oxalic acid.

	a_1	a_2	b_1	b_2	c_2	c_3	c_4	c_5
$u(C-C')$	0.0506(0.0030)	0.0526(0.0048)	0.0535(0.0030)	0.0551(0.0051)	0.0515(0.0049)	0.0454(0.0038)	0.050	0.003
$u(C=O_2)$	0.0399(0.0013)	0.0361(0.0020)	0.0391(0.0013)	0.0350(0.0022)	0.0371(0.0020)	0.0364(0.0013)	0.040	0.011
$u(C-O_1)$	0.0484(0.0014)	0.0448(0.0022)	0.0476(0.0014)	0.0438(0.0023)	0.0458(0.0022)	0.0459(0.0013)	0.054	0.020
$u(C\cdots O_2')$	0.0747(0.0080)	0.0742(0.0100)	0.0921(0.0224)	0.0708(0.0246)	0.0683(0.0088)	0.0617(0.0149)	0.082	0.005
$u(C\cdots O_1')$	0.0674(0.0052)	0.0681(0.0080)	0.0592(0.0040)	0.0691(0.0160)	0.0602(0.0059)	0.0445(0.0077)	0.098	0.010
$u(O_1\cdots O_2)$	0.0620(0.0023)	0.0597(0.0030)	0.0598(0.0038)	0.0572(0.0045)	0.0584(0.0032)	0.0562(0.0010)	0.100	0.020
$u(O_2\cdots O_2')$	0.0746(0.0074)	0.0763(0.0064)	0.0770(0.0087)	0.0774(0.0078)	0.0774(0.0083)	0.0756(0.0157)	0.082	0.002
$u(O_1\cdots O_2')$	0.1131(0.0033)	0.1139(0.0042)	0.1120(0.0038)	0.1119(0.0043)	0.1150(0.0043)	0.1123(0.0065)	0.169	0.015
$u(O_1\cdots O')$	0.1285(0.0169)	0.1183(0.0193)	0.1224(0.0174)	0.1173(0.0192)	0.1251(0.0175)	0.1110(0.0230)	0.097	0.002

Root mean-square amplitudes of vibration, $u=\langle \varDelta z^2\rangle^{\frac{1}{2}}$ (Ref. 30) and $K=(\langle\varDelta x^2\rangle+\langle\varDelta y^2\rangle)/2r$ in Å, a_1-c_3 are experimental values obtained by least-squares in the same refinements as in Table 1. In c_4 are given u-values computed for an approximate valence force field and in c_5 the corresponding K-values.[16] These values for the distances involving hydrogen atoms are (u, K): $r(H-O_1)$ (0.076, 0.035), $r(C\cdots H)$ (0.121, 0.042), $r(C\cdots H')$ (0.192, 0.029), $r(H\cdots O_2)$ (0.120, 0.033), $r(H\cdots O_2')$ (0.263, 0.0041), $r(H\cdots O_1')$ (0.185, 0.009), and $r(H\cdots H')$ (0.223, 0.015).

Using the scale factors from the least-squares refinement, the two curves were again connected, and radial distribution functions and autocorrelation power spectra [15] were computed. These results are illustrated in Fig. 3.

Cyvin [16] has computed u- and K-values for oxalic acid at 160°C from an estimated valence force field, refined to agree with the insufficient number of assigned normal frequencies available for oxalic acid.[17] His results are included in Table 2.

DISCUSSION

The structure investigation. As results of the IR and electron diffraction investigation, it was found that free oxalic acid possesses a planar *trans* conformation with weak intramolecular hydrogen bonds to the carbonyl oxygens at the neighbouring carboxyl groups. To study how well this model fits the data, the effects on the standard deviations from correlated errors in the intensities, and the reliability of the standard deviations, the results of several least-squares refinements are given in Table 1 and 2.

Comparing the results in column a_2 and b_2 of the two tables, the parameters obtained with the geometry of the model as restraint, a_2, agree satisfactorily with the parameters determined as independent variables, b_2. The two square error sums show that it would be difficult to find another model which fits the data much better than the applied one.

If the computed u- and K-values [16] are used to transfer the r_a distances to r_α ones,[18] demanding that the r_α-distances satisfy the geometry, the agreement is slightly poorer than when the r_a distances themselves fulfill the geometry. The r_α distances should be a better approximation of the average structure at the applied nozzle temperature and thereby be in better agreement with the geometry than the r_a distances. As mentioned, the valence force field used to compute the u- and K-values may be inaccurate, and the intramolecular hydrogen bonds were not included in this force field.[16] Comparing the experimental u-values with the computed ones, the former are in most cases smaller than the latter, indicating that the applied force field may not have been sufficiently accurate to properly transfer r_a distances to r_α ones. Therefore the best values of the parameters are the ones given in column a_2 of the two tables.

Fig. 3 shows that several of the distances are closely spaced and the parameters should therefore be correlated. For the planar *trans* model, ϕ_1 and ϕ_2 are correlated with a coefficient of $\varrho_{\phi_1,\phi_2} = -0.98$. For refinements with no geometric restraint, the following terms of the moment matrix of the parameters are large: $\varrho_{r(C\cdots O_1'),\ r(C\cdots O_1')} = -0.96$, $\varrho_{r(C\cdots O_1'),\ r(O_1\cdots O_2)} = 0.75$, and $\varrho_{r(O_1\cdots O_1'),\ r(O_2\cdots O_2')} = -0.89$. Several of the u-values are also strongly correlated. In spite of this correlation, the least-squares iteration converges for the distances and u-values not involving hydrogen atoms from a sufficiently close starting vector even when no geometric restraint is applied. That the data obviously contain enough information to split the closely spaced distances is also demonstrated by the autocorrelation power spectrum representation of the data [15] illustrated in Fig. 3. The agreement between the spectrum of the experimental data with the spectrum of the model should confirm that the least-squares iteration has not been trapped in a secondary minimum. It

should be noted that when several distances are closely spaced, the maxima in the autocorrelation power spectrum are shifted from the correct distance values.

If a parameter is determined from the data from one plate for each of the two camera distances with the value r_{ki}, and the average value of this parameter from the $q = 4$ data sets is r_k, the standard deviation of the parameter is then estimated by

$$[\sum_{i=1}^{q}(r_{ki} - r_k)^2/q(q-1)]^{\frac{1}{2}}$$ (2)

Results for the average parameters and their standard deviations estimated in this way are given in column c_3 of Tables 1 and 2. For the geometric param- eters and the less accurately determined u-values, the standard deviations obtained in this way seem somewhat larger than the least-squares standard deviations for a weight matrix including off-diagonal terms due to correlation in the data, while for the most accurately determined u-values, the least squares standard deviations for a diagonal matrix seem to be in better agreement with the values obtained from eqn. 2.

In the least-squares refinements, the standard deviations of the parameters are estimated by $\sigma_0 \sqrt{(B^{-1})_{ii}}$ with $\sigma_0 = (V'PV/(n-m))^{\frac{1}{2}}$. For the least-squares refinements using a weight matrix including off-diagonal elements, this way to estimate σ_0 gives a value of 2.7, in relatively good agreement with the value of 2.1 obtained from the data of the 20 cm camera distance, but somewhat larger than the value of 1.4 from the 48 cm distance data. It is also seen from the difference curves in Fig. 1 that the absolute values of the differences be- tween the experimental data and the computed intensities for the 20 cm data are of the same magnitude as the standard deviations in each point, σ_j, while for the data from the 48 cm camera distance, the σ_j's are smaller than the absolute values of the differences between the two intensities. Estimations of standard deviations from only four measurements are of course uncertain, but it might be hoped that doing the same type of investigations for several molecules instead of collecting a larger set of data for a single one, a significant pattern will appear.

The results obtained in the present work indicate that for most of the parameters, the standard deviations obtained for a weight matrix including off diagonal elements due to correlated errors are more realistic than the standard deviations obtained for a diagonal weight matrix. For the data from the 48 cm camera distance, the agreement with the theoretical intensities are not as good as one would expect from the estimated standard deviations of the data. This must be due to systematic errors in the data or that the applied theory is not sufficiently accurate. These results are consistent with results obtained previously,[3] and the estimates of the standard deviations obtained by the least-squares method are still uncertain. They may be too small for some or all of the parameters.

The electron wavelength was based upon diffraction from gold. If reference instead is made to gaseous CO_2, the distance values should be reduced by about 0.25 %.[25]

The molecular structure and comparison to the structure of related molecules.
The present work confirms the conclusion of the earlier electron diffraction
investigation.[4] The reason why the free molecule has a planar *trans* conforma-
tion is probably complex. This planarity is not caused by conjugation of the
double bonds, as the $C-C$ distance of 1.548 (0.004) Å is typical for a single
bond. Conjugation in the system may be hindered by the electronegativity
of the oxygen atom,[1] and the result for oxalic acid is in agreement with the
decreasing $C-C$ bond order in the series butadiene, acrolein, and glyoxal
(1.463, 1.478, and 1.525 Å).[19] Several molecules similar to oxalic acid have
planar *trans* conformations without shortening of the $C-C$ central bonds:
oxalyl chloride,[20] dimethyl oxalate,[21] and oxamide.[22] Also the group
$C(OH)COOH$ is *trans*-planar in the crystals of some hydroxyacids despite
that van der Waals and dipole interactions are not favourable to this arrange-
ment.[23]

The hydrogen bonds between the neighbouring carboxyl groups should
also contribute to the stability of the planar *trans* form of oxalic acid. The
$r(O_2 \cdots O_1')$-distance of 2.717 (0.005) Å and the geometry of the five-membered
ring closed by a hydrogen bond are favourable, and similar types of intra-
molecular hydrogen bonds have been reported.[7,24] Hydrogen bonds of this
type have usually smaller shifts in the $O-H$ stretching frequency than the
corresponding linear ones. The observed shift for oxalic acid is 225 cm^{-1},

Table 3. Structure parameters of oxalic acid from the present investigation compared to the
results of some recent studies of oxalic acid and of monomer and dimer formic acid.

	Gaseous state			Solid state	
	HCOOH[a]	(COOH)$_2$[b]	(HCOOH)$_2$[c]	(COOD)$_2 \cdot 2D_2O$[d]	α-(COOH)$_2$[e]
$r(C-C)$		1.548(0.004)		1.539(0.005)	1.560(0.010)
$r(C=O)$	1.217(0.003)	1.208(0.001)	1.220(0.003)	1.201(0.004)	1.194(0.007)
$r(C-O)$	1.361(0.003)	1.339(0.002)	1.323(0.003)	1.300(0.004)	1.289(0.006)
$r(O-H)$	0.984(0.024)	1.056(0.014)	1.036(0.017)	1.042(0.008)	
$\angle C-C=O$		123.1(0.9)		122.3(0.3)	122.7(0.5)
$\angle O=C-O$	123.4(0.5)	125.0(0.2)	126.2(0.5)	126.2(0.3)	128.1(0.6)
$\angle C-O-H$	107.3(4.4)	104.4(2.3)		112.3(0.5)	
ν_{O-H}	3570	3475	3110	2497	3114

Distances in Å and angles in degrees. ν_{O-H} is the wavenumber of the $O-H$ stretching vibra-
tion bands in cm^{-1}.
a. Monomer formic acid studied by gas electron diffraction.[25] ν_{O-H} is taken from Ref. 28. Note
   that for monomer and dimer formic acid an estimate of contributions from error in the electron
   wavelength has been added to the standard deviations. As this has not been done in the present
   work, these standard deviations are not directly comparable.
b. Oxalic acid, this investigation.
c. Dimer formic acid studied by gas electron diffraction.[25] ν_{O-H} is taken from Ref. 29.
d. Deuterated oxalic acid dihydrate studied by X-ray diffraction [26] and neutron diffraction.[27]
   ν_{O-H} is from Ref. 3, and the value for the hydrogen substituted compound is given. The value
   of ν_{O-D} is 1940 cm^{-1}.[3]
e. α-Oxalic acid studied by X-ray diffraction.[1] ν_{O-H} is taken from Ref. 3.

while for a corresponding linear hydrogen bond a shift of 730 cm^{-1} would be expected.[7]

In Table 3, the structure parameters of oxalic acid are compared to the X-ray result for α-oxalic acid[1] and to the X-ray[26] and neutron diffraction[27] results for deuterated oxalic acid dihydrate. Included in the table are also results for monomer and dimer formic acid from a recent electron diffraction reinvestigation by Bastiansen et al.[25] Most interesting is perhaps the variation in the C−O bond lengths in these molecules. For the three free molecules and the deuterated dihydrate of oxalic acid, this bond length is shorter the more strongly the attached hydrogen atom is involved in hydrogen bond formation as demonstrated by the variations in the O−H stretching frequencies also included in the table. The results for α-oxalic acid do not fit into this picture. According to the connection between the O···O distances and the O−H stretching frequencies for linear hydrogen bonds in crystals, the O···O separation in α-oxalic acid of 2.71 Å[1] should correspond to an O−H frequency of 2950 cm^{-1},[7] and with the given standard deviation of 0.006 Å for the C−O bond it is difficult to judge if the results for this molecule are significantly in disagreement with the trend suggested by the four more recently investigated structures. Also the O=C−O angles are larger for a shorter C−O distance.

The effects from the hydrogen bond environment on the carbonyl distance do not seem to be that important, as these distances are significantly different neither in monomer and dimer formic acid nor in the three different forms of oxalic acid. Going from formic to oxalic acid, however, the carbonyl distance decreases slightly.

Finally, comparing the distances in free oxalic acid to the two results for the solid compounds, no significant differences are observed except for the already mentioned variations in the C−O distances. The about 8° smaller C−O−H angle in the free molecule than in the deuterated dihydrate is reasonable as a smaller value of this angle would bring the hydrogen atom closer to the neighbouring carbonyl oxygen, thereby strengthening the intramolecular hydrogen bond.

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